

Equilibrium and Nonequilibrium Properties of Bulk and Nanosize Clusters of Carbon

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Motivations and introduction

Many equilibrium properties of carbon, such as the graphite-diamond phase line, are well established. Nevertheless, many issues at high pressure and temperature still remain unresolved. For example the location of the graphite-diamond-liquid triple point is only known to within 10%. For the diamond melting line, all that is known is that it has a positive slope.

Our knowledge of nonequilibrium properties of carbon is even more dismal. For example, thermochemical calculations of the detonation velocity of TNT (which is a carbon-rich explosive) differs from experiment by as much as 5%. This difference may be attributable to yet unidentified metastable processes involving nanometer size clusters of carbon formed during detonation.

The equilibrium aspect of the present work involves thermodynamics of phase changes in carbon within heretofore unexplored pressure and temperature regimes. The nonequilibrium aspect of the present work is to understand coagulation of carbon clusters and also the dynamics of phase changes between graphitic and diamond clusters. One theoretical tool which is useful for both studies is the molecular dynamics simulation method.

On the equilibrium side, we explored the phase diagram of carbon at high temperature and pressure via molecular dynamics using the bond order potential developed by Brenner [1]. This potential has been used successfully to model the growth and mechanical properties of thin amorphous carbon films [2]. It is extremely powerful in that it allows for realistic chemical breaking and formation of bonds and reproduces correct bond strengths for many bonding possibilities found in hydrocarbon systems, including correct structures for all the common hybridization states (sp , sp^2 and sp^3) of carbon under ambient condition and allowance for the breaking and formation of covalent bonds. The particular features examined are the diamond melting line, the graphite melting line and the local structure of the liquid phase.

However, the Brenner potential was optimized for normal temperatures and pressures. In addition, the potential as presently developed has neglected the long-range van der Waals forces which may be important for holding graphitic sheets together. Possible improvement on the Brenner potential in this connection will be discussed.

Next, we have examined the phase stability of nanometer size clusters of carbon atoms using *ab initio* and the semiempirical MNDO method with AM1 and PM3 parameterizations. The calculations were carried out for both graphite and diamond clusters of various sizes, in which the 'surface' carbon atoms either have 'dangling' bonds or are saturated with hydrogen. Calculations considered as many as nearly 300 carbon atoms. Resulting cluster energies are represented as a simple analytic function of the cluster size. This information provides the relative stability and their energy of formation of graphite and diamond clusters as a function of cluster size.

The height of the reaction barrier for the graphite to diamond transition and the heat of formation of carbon clusters are needed for the study of the graphite-to-diamond transformation

kinetics and the coagulation kinetics of carbon, respectively. Previous calculations in this regard were done only for infinite-sized systems [3]. Similar results for finite systems are needed. This was done by computing the energy to convert the sp^2 bonding to sp^3 for two initially stacked graphitic layers along the 'reaction path', obtained under the linear synchronous transit approximation. It assumes that any point on the reaction path can be defined by a mixture of reactant (sp^2 graphite) and product (sp^3 diamond) geometry.

Carbon coagulation occurs through diffusion of carbon clusters described above. Their growth kinetics have been examined by solving a simplified version of Smoluchowski equations,

$$dc_k/dt = \sum_{i+j=k} k_{ij}c_i c_j - 2c_k \sum_j k_{jk}c_j,$$

where k_{ij} describes the rate constant for coagulation of cluster i with concentration c_i and cluster j with concentration c_j . Use of a simplified approximation on k_{ij} provides a simple analytic expression for c_i .

We have implemented the above carbon clustering kinetics in a multi-phase multi-component chemical equilibrium code, so that it can account for a time-dependent surface correction to the Gibbs free energy of diamond and graphite clusters at a given time. Applications to TNT show that the new model can reliably predict the overdriven shock wave data and the detonation velocity data with various initial densities. Results from this study will provide important inputs to understanding the performance of carbon-rich explosives.

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References

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